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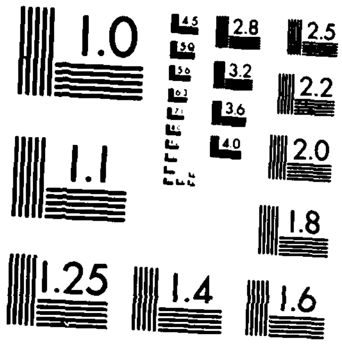

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Rapid-scan infrared spectroscopy studies of the high rate thermolysis of energetic molecules containing CNO_2, NNO_2, ONO_2, N_3, NO_3^-, ClO_4^- and furoxan groups are reported. In addition, solid-solid phase transition studies by IR spectroscopy, DSC, solid-state NMR and X-ray crystallography have been conducted. Structure/property/reactivity relationships have been established for the formation of NO_2 and HONO. Understanding of some of the factors influencing the formation of CH_2O, N_2O and NO has also been acquired. The influence of the static applied pressure on the first observed decomposition products has been explored successfully.

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I. Research Objectives

The objectives of this research program are multifold. First, little is known about the chemical species contained in the dark zone that interfaces the surface of the condensed phase and the flame of a burning propellant. The problem is that in practice this transient zone is so thin that it has resisted diagnostic analysis. We are attempting to simulate this region by heating a solid material very rapidly under realistically high pressures without actually creating the flame. By the use of unusually fast scanning IR spectroscopy, the gas products that are ejected immediately above the surface can be identified and quantified. Since it is these gas products that feed the flame, this work also in effect simulates ignition chemistry.

Second, we are attempting to construct structure-property-reactivity relationships for the thermolysis of a wide variety of energetic materials. Such relationships would allow qualitative predictions of the initial gas products that are released on rapid thermolysis simply by examining the structure or measuring a particular physical property. Establishing such relationships is also a goal in other sectors of science such as the pharmaceutical industry and the catalysis industry. It should be possible to construct these relationships for the products initially liberated by the thermal decomposition of an energetic material.

Third, we are attempting to uncover the solid-solid phase transition patterns of energetic materials since solid-solid phase transitions influence the efficacy of handling and use of energetic materials. This work includes molecular structure studies by x-ray crystallography, thermal analysis studies by DTA, and phase transition-structural analysis by variable temperature IR spectroscopy. Kinetic data can sometimes be acquired for these phase transitions.

II. Status of Research

A. Development of new techniques

Rapid-scan infrared spectroscopy studies combined with fast pyrolysis methods developed in house is progressing well. Already a vast amount of new information and new levels of understanding of the decomposition processes of energetic materials have emerged.

Several generations of a homebuilt high-rate pyrolysis cell have been developed which now permit the observation and quantitation of gas products produced at heating rates of 10-250 K sec^{-1}. These products can be monitored as a function of time as evidence of further reactions among the products. While this facility is currently unsurpassed in the world for doing these sorts of experiments, we are not planning to rest on it. For instance, we are currently designing a residual gas analyzer system to permit combined infrared analysis and mass spectrometric analysis of the products. This procedure will allow quantitation of both IR active and IR inactive products, as well as helping to identify products we occasionally see that cannot be identified by IR spectroscopy alone.

We are planning to add pressure to temperature as a variable in our condensed phase studies. This will be done with a heated diamond anvil cell.

B. Thermal Decomposition

A large amount of research has been conducted and written up during the initial year of this program. Product speciation for about 50 compounds (Figure 1) as a function of heating rate (up to 250K sec^{-1}) and pressure (1-1000 psig) has been assembled so far. Common conditions have been used in almost all cases so that the data from one compound can be directly compared to that of another. Several patterns have begun to emerge and are summarized below.

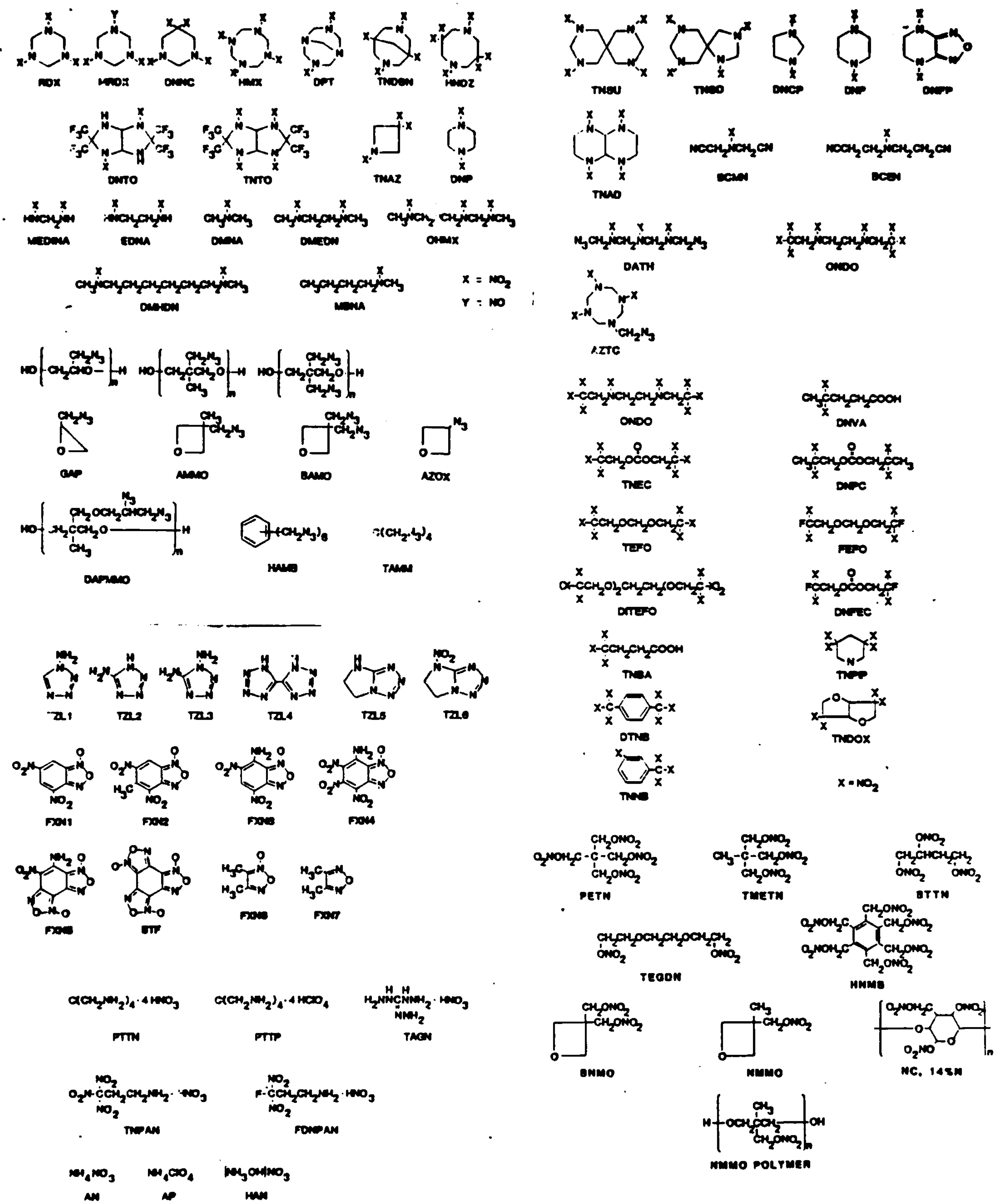


Figure 1. Compounds studied to date in this program.

(1) Segmented decomposition patterns have been observed in nitrate esters wherein three classes of compounds emerge: those for which side chain products dominate, those for which side chain and backbone products compete, and those for which backbone products dominate.

(2) Convincing evidence that decomposition preceeds deflagration in high heating rate thermolysis experiments has been obtained. This comes from capturing the transition from decomposition products to deflagration products in the same experiment on gem-trinitro and gem-fluorodinitro compounds. A representative result is shown in Figure 2.

(3) The asymmetric stretching frequency of the $-NO_2$ group in C_2NNO_2 containing nitramines is a good diagnostic of whether NO_2 will be the dominant decomposition product or will be mixed with comparable concentrations of other products. This correlation is shown in Figure 3.

(4) Compounds containing the $O_2NN-CH_2NNO_2$ fragment very frequently produce N_2O and CH_2O upon thermolysis. The exception so far is DNNC where the $C(NO_2)_2$ fragment seems to dominate the decomposition.

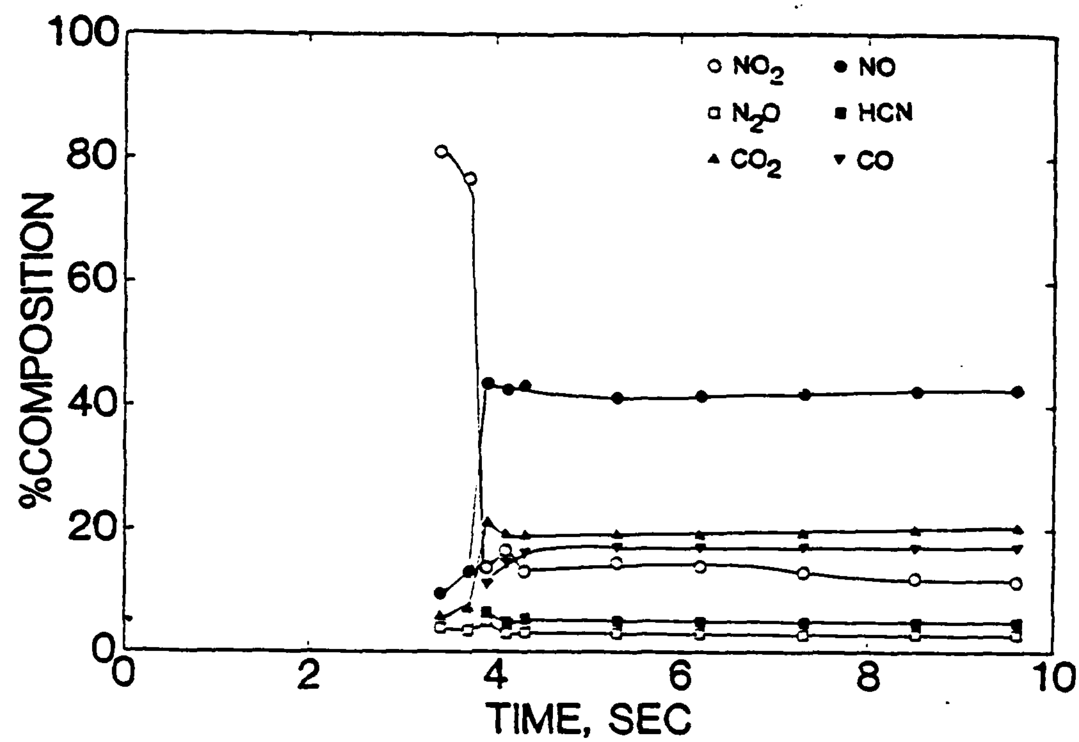
(5) Nitramines almost always liberate HONO as one of the thermolysis products whereas few other energetic materials do.

(6) Primary alkylamine nitrate salts appear to decompose initially by proton transfer leading to HNO_3. The HNO_3 thus produced then oxidizes the alkylamine. The equivalent proton transfer reaction does not occur with secondary or tertiary alkylamines.

(7) Solid-solid phase transitions among various polymorphs were discovered and studied for DNNC, TAGN, TNDBN, and DPT. TNDBN provides an example of a variation on conformational polymorphism which is an interesting and important phenomenon for HMX.

Figure 2

The concentration-time profile of the gas products from FEFO heated at $100K\ sec^{-1}$ under 65 psi of Ar.



Initial thermal reaction is decomposition by C-N bond fission.

$$-\overset{|}{\underset{|}{C}}-NO_2 \xrightarrow{\Delta} NO_2 + \text{residue}$$

Follow-up step is vigorous oxidation of the remainder of the molecule by NO_2 to produce NO and deflagration products.

$$NO_2 + \text{residue} \xrightarrow{\Delta} CO_2 + NO + \text{other products}$$

This figure demonstrates that decomposition occurs in advance of deflagration when a material is heated at a high rate. This may seem self-evident but it is devilishly difficult to prove and has not been proven before in real time as far as we are aware.

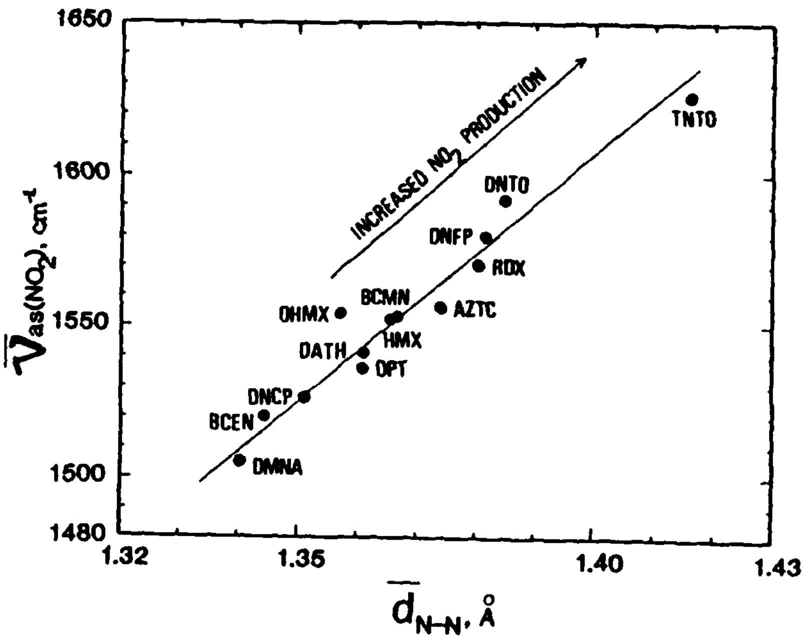


Figure 3. A structure-property-reactivity relationship for secondary nitramines (C_2NNO_2) showing the correlation of the asymmetric NO_2 stretching frequency with the N-N bond distance. Compounds to the upper left are strong NO_2 generators.

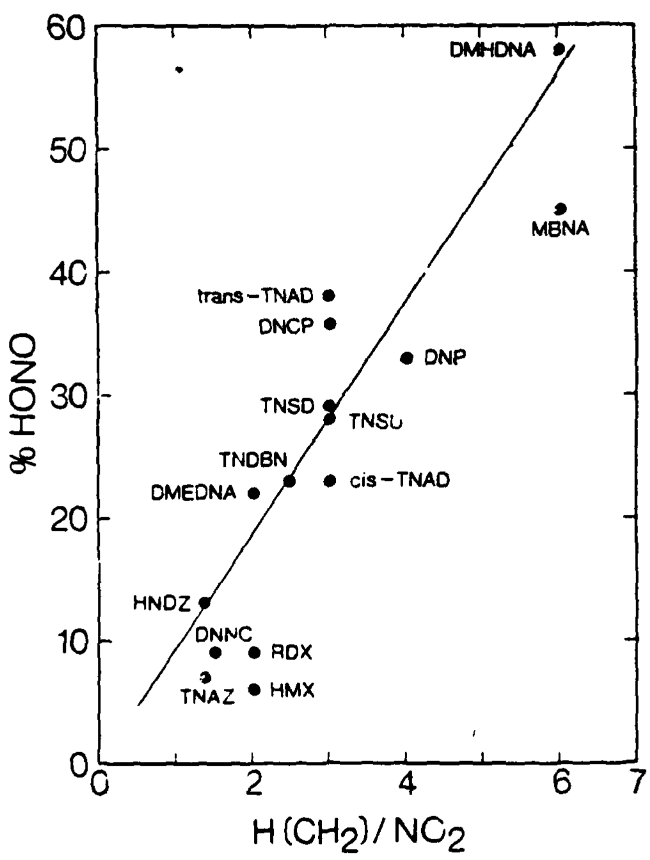


Figure 4. The relative % HONO produced in the initial 0.2 sec when nitramines are heated at $dT/dt = 120\text{-}140\ K\ sec^{-1}$. There is a correlation with the H• to NO_2• ratio in the parent molecule.

(8) The decomposition of polymeric azide-containing compounds is relatively independent of pressure in the 1-1000 psig range suggesting that their decomposition pattern is dominated by a single process, probably decomposition of the azide group to the nitrene and N_2.

(9) The routine observation of HONO being liberated upon thermolysis of nitramines has permitted some understanding of its formation from the condensed phase. Rather than being formed by a concerted four or five-centered elimination step, HONO forms in the condensed phase largely by adventitious contact between $H^\bullet$ and $NO_2^\bullet$. The larger the H/NO_2 ratio in the parent molecule, the more HONO that is produced. Figure 4 shows this correlation.

(10) Primary nitramines were found to be strong N_2O generators while linear secondary nitramines produce much less N_2O and more NO_2 or HONO. The $>NCH_2N<$ unit is less thermally stable than the $>NCH_2CH_2N<$ unit.

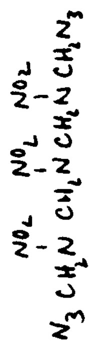
(11) For mixed azidomethyl-nitramines, it has been possible to show that the azide group decomposes first and probably produces a radical that depolymerizes to N_2O and CH_2O. The N-N bond fission process in such molecules is strongly suppressed.

(12) Linear and cyclic nitramines were found to have comparable patterns of decomposition.

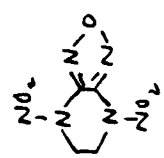
C. Solid Phase Studies

Crystal structure determinations were undertaken on the compounds shown below:

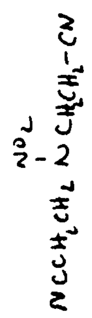
DATH



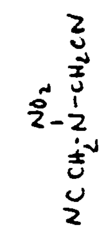
DNFP



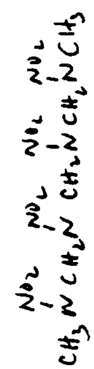
BCEN



BCMN



OHMX



These studies augmented our work on trying to put some organization into the complex solid-solid phase transition patterns that are exhibited by various energetic materials. This is a very ambitious project which, not surprisingly, has been somewhat less successful than that described above at putting structure-property-reactivity relationships of energetic materials on a more sound footing. A preliminary and rather crude correlation of the enthalpy of the lower temperature solid phase with the molecular weight separates compounds according to whether they are cyclic or acyclic in their backbone.

III. Interactions

A. Meeting and Seminars

(1) Pittsburgh Conference on Analytical Chemistry, Atlantic City, NJ, for equipment examination, March 1986

(2) National American Chemical Society Meeting, New York, NY for Symposium on Vibrational Spectroscopy of Polymers, March 1986

(3) Los Alamos National Laboratory, August 1986 for intensive two day discussion on energetic materials

(4) Nitramine Workshop, sponsored by ARO, Livermore, CA, June 1986

(5) MICOM, Marshall Space Flight Center, and Thiokol-Huntsville, March, 1986 for intensive discussions on energetic materials

(6) AFOSR/AFRPL Rocket Propulsion Research Meeting, Lancaster, CA, September 1986.

B. Substantive Interactions with Other Laboratories During Year

The nature of this work requires that I regularly talk with synthesis chemists and persons involved in the characterization of thermally labile compounds. Through the past year of this program, interactions have been developed with the following persons (no particular order is meant).

Naval Surface Weapons Center-White Oak
- Horst Adolf

Sandia Livermore National Laboratory
- Carl Melius
- Rich Behrens
- Sheridan Johnston
- Steve Vosen
- Rob Armstrong

Naval Surface Weapons Center-Indian Head
- George Nauflett

Picatinny Arsenal
- Surya Bulusu
- Frank Owens
- Arthur Bracuti
- Everett Gilbert
- Gilbert Sollott
- Yvon Carignan

Ballistics Research Laboratory
- Andrzej Mizolek
- Robert Fifer
- Mike Schroeder
- Nate Klein
- Eli Freedman
- Dick Beyer

Los Alamos National Laboratory
- Mike Coburn
- Jim Ritchie
- Ray Rogers
- Steve Agnew
- Carl Storm
- Jerry Dick

Lawrence Livermore National Laboratory
- Raymond McGuire
- Cliff Coon

Naval Research Laboratory
- Robert Doyle
- Richard Gilardi

Stanford Research International
- Cliff Bedford
- Dave Golden
- Dave McMillan

Lawrence Berkeley National Laboratory
- Yuan Lee

Aerochem
- Don Olson

Rocketdyne
- Dean Woolery
- Milt Frankel
- Joe Flanagan
- Jim Weaver
- Carl Christie

Aerojet
- Gerry Manser
- Mike Todd
- Fred Meyers

United Technologies
- D. Guimont

Morton-Thiokol, Elkton
- Rod Willer
- Ernie Sutton
- Winston Brundige
- Frank Goetz
- Richard Biddle

Morton-Thiokol, Wasatch
- Dave Flanigan
- Thomas Davidson

Morton-Thiokol, Huntsville
- William Graham
- Jim Hightower

Hercules-Aerospace
- Robert Earl
- Kenneth McCarty
- Mark Trygstad

Fluorochem
- Kurt Baum

Georgia Tech
- Ed Price

University of Colorado
- Mel Branch

Renssalear Polytech Institute
- Arthur Fontijn

Purdue University
- John Osborne

Systems Research Laboratory
- Larry Goss

Nippon Fats & Oils (Rocket Propellant Section)
- Kenji Saumikawa
- Koichiro Uchiyama

Office of Naval Research
- Dick Miller

Institute of Space & Astronautical Science (University of Tokyo)
- Akira Iwama

3rd Japan Defense Agency, Tokyo
- N. Kubota

Fraunhofer Institute, Karlsruhe
- A. Pfeil
- H. Schmidt

Defense Research Center, Adelaide
- T. T. Nguyen

MICOM
- Walt Wharton
- Bill Stevens

Other:

1. Reviewed proposals on Energetic Materials for:

   Army Research Office
   National Science Foundation
   Ballistics Research Laboratory

IV. Publications

1. Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 9. Polymorphism, Crystal Structures, and Thermal Decomposition of Polynitroazabicyclo[3.3.1]nonanes," J. Phys. Chem., 90, 2526 (1986).

2. T. B. Brill and Y. Oyumi, "Thermal Decomposition of Energetic Materials 10. A Relationship of Molecular Structure and Vibrations to Decomposition: Polynitro-3,3,7,7-tetra(trifluoromethyl)-2,4,6,8-tetraazabicyclo(3.3.0)-octanes," J. Phys. Chem., 90. 2526 (1986).

3. Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 11. Condensed Phase Structural Characteristics and High Rate Thermolysis of Di- and Trinitroaliphatic Carboxylic Acids and Carbonates," Combust. & Flame, 65, 103 (1986).

4. Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 12. Infrared Spectral and Rapid Heating Rate Thermolysis Studies of Azide-Containing Energetic Monomers and Polymers," Combust. Flame, 65, 127 (1986).

5. Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 13. High Rate Thermolysis of Benzofuroxans and 3,4-Dimethylfuroxan," Combust. Flame, 65, 313 (1986).

6. Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 14. Partially-Segregated Decomposition Detected in Rapid, Real-time Thermolysis of Nitrate Esters at Various Pressures," Combust. Flame, in press.

7. Y. Oyumi and T. B. Brill, "On the Lineshape of $\nu_{as}(NO_2)$ in Nitrate Esters: 3,3-Bis(nitratomethyl)oxetane," Spectrochim. Acta, 42A, 1001 (1986).

8. Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 15. Evidence that Decomposition Initiates Deflagration: High-rate Thermolysis of FEFO, TEFO, and DITEFO," Prop. Explos. Pyrotech., 11, 35 (1986).

9. Y. Oyumi, A. L. Rheingold and T. B. Brill, "Thermal Decomposition of Energetic Materials 16. Solid Phase Structural Analysis and the Thermolysis of 1,4-Dinitrofurazano[3,4-b]piperazine," J. Phys. Chem., 90, 4686 (1986).

10. T. B. Brill and Y. Oyumi, "Thermal Decomposition of Energetic Materials 18. A Relationship of Molecular Composition to HONO Formation: Bicyclo and Spirotetranitrotetranitramines," J. Phys. Chem., in press.

11. Y. Oyumi, A. L. Rheingold, and T. B. Brill, "Thermal Decomposition of Energetic Materials 19. Unusual Condensed Phase and Thermolysis Properties of a Mixed Azidomethylnitramine: 1,7-Diazido-2,4,6-trinitrazaheptane, J. Phys. Chem., submitted.

12. Y. Oyumi, T. B. Brill, and A. L. Rheingold, "Thermal Decomposition of Energetic Materials 20. A Comparison of the Structural Properties and Thermal Reactivity of an Acyclic and Cyclic Tetramethylenetetranitramine Pair, Thermochim. Acta, in press.

13. Y. Oyumi and T. B. Brill, "Thermal Decomposition of Energetic Materials 21. The Effect of the Backbone Composition of the Products Evolved Upon Rapid Thermolysis of Linear Nitramines," Combust. Flame, in press.

14. Y. Oyumi, A. L. Rheingold and T. B. Brill, "Thermal Decomposition of Energetic Materials 17. Bis(cyanomethyl)nitramine and bis(cyanoethyl)-nitramine," Prop. Explos. Pyrotech., submitted.

V. Research Participants

A. Principal Investigator

Thomas B. Brill

B. Faculty Collaborators (University of Delaware)

Arnold L. Rheingold (X-Ray Crystallography)
Burnaby Munson (Mass Spectrometry)
Cecil Dybowski (Solid State NMR Spectroscopy)

C. Graduate Students

1. Full Effort

Yoshio Oyumi	Ph.D.	Expected December 1986
Jeff Kiley		
Tom Russell		

END

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